

CARNEGIE-MELLON UNIVERSITY
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INVESTIGATION OF STRESS CORROSION CRACKING OF TITANIUM ALLOYS

Semi-Annual Progress Report No. 6

for the Period

December 1, 1968 through May 31, 1969

BY

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TABLE OF CONTENTS

	Page
ABSTRACT	1
INTRODUCTION	2
MATERIALS AND PROCEDURES	3
EXPERIMENTAL RESULTS AND DISCUSSION	5
Effect of Halide Concentration and Methanol Purity on Cracking Susceptibility	5
Effect of Solution Composition on S.C.C. Behavior of Ti-6Al-4V Under Applied Anodic and Cathodic Polarization Currents	8
Effect of Pre-Corrosion on the S.C.C. Behavior of 99.5 Ti and Ti-6Al-4V	13
Failure of Crystal Bar Titanium in Methanolic Solutions . .	15
S.C.C. of Rod Specimens	16
Fractographic Examination of Rod and Foil Specimens	17
CONCLUSIONS	20
FUTURE WORK	21
REFERENCES	22

ABSTRACT

Annealed foil specimens of crystal bar titanium are susceptible to failure when stressed in methanolic solutions, and break in similar times to annealed foil specimens of the lower purity 99.5 Ti. The failure of annealed specimens of 99.5 Ti is due to a grain boundary corrosion mechanism, whereas the evidence would seem to favor a more complicated stress corrosion cracking mechanism for the failure of Ti-6Al-4V. Results obtained from polarization studies on Ti-6Al-4V may be used to support the existence of a protective film under conditions of cathodic polarization. Rod specimens of Ti-6Al-4V are equally as susceptible to failure as foil specimens of the same nominal composition.

Fractographic evidence indicates the existence of a brittle, discontinuous cracking mechanism in the transgranular failure of stressed titanium alloy specimens in methanolic solutions.

INTRODUCTION

The progress of the last six months is herewith reported. A summary of the accomplishments of this program during the first one and a half years was presented in Semi-Annual Progress Report No. 4. In the interim period (one year) a continued investigation of the alloys 99.0 Ti, 99.5 Ti, Ti-5Al-5Sn-5Zr, Ti-6Al-4V and Ti-13V-11Cr-3Al, in methanolic solutions was undertaken. The main lines of investigation were directed towards studies of the inhibiting effect of organic additions, the effects of variation in solution temperature, corrosion effects, effects of "impurity" contents of the methanolic solutions on cracking susceptibility, and electrochemical effects.

Research in the subsequent period has continued the studies of effects of solution "impurity" contents on cracking susceptibilities. In addition, a high purity grade of titanium, crystal bar titanium, has been tested. Work attempting to differentiate between S.C.C. (stress corrosion cracking) and corrosion effects in the failure of 99.5 Ti and Ti-6Al-4V has been carried out. In addition, the behavior of Ti-6Al-4V under applied polarization conditions as a function of solution composition, has been extensively investigated. Rod specimens (0.136" diameter) of Ti-6Al-4V and Ti-5Al-5Sn-5Zr have also been tested to compare with the results obtained from the more usually tested foil specimens (~ 0.003" thickness) of the same nominal composition.

A preliminary fractographic study has been made of alloy specimens which have failed in methanolic solutions during the course of the program, using a scanning electron microscope.

MATERIALS AND PROCEDURES

Work has been continued on the alloys, 99.5 Ti, Ti-0.2 Pd, Ti-5Al-5Sn-5Zr, Ti-6Al-4V and Ti-13V-11Cr-3Al, whose chemical compositions in weight percent are given in Table I. Also, specimens of Ti-6Al-4V and Ti-5Al-5Sn-5Zr have been tested in rod form (0.136" diameter) as well as in the more usual foil form (approximately 0.003" thickness). In addition, a sample of titanium crystal bar has been received whose detailed analysis is given in Table II.

Cylindrical tensile test pieces were machined from the 3/8" diameter rod, the overall length was 2.7", the gauge length 1.5" and the gauge diameter 0.136". Following machining, the Ti-6Al-4V specimens were given a stress relieving treatment of 2 hours at 1110°F followed by air cooling; the Ti-5Al-5Sn-5Zr specimens were given an annealing treatment of 1 hour at 1600°F followed by air cooling. Heat treatments were performed in sealed vycor tubing under a partial pressure of helium. The specimens were strained in tension on an Instron hard beam testing machine, the necessary total strain being applied over a period of about 30 seconds, after which the moving crosshead was locked in position. The solution was then added to a polyethylene dish through which the specimen was threaded, leakage being prevented by a plug of paraffin wax, and the load relaxation recorded.

The titanium crystal bar was cold rolled without annealing down to 0.0075" thickness, giving a reduction of not less than 95%. The resulting strip was sheared to 1/4" wide specimens which were then sealed in vycor under a partial pressure of helium, and given an annealing treatment of 1 hour at 1295°F followed by air cooling.

The tensile properties of the foil and rod specimens are given in Table III. The ultimate tensile strength and 0.2% offset yield strength are reported in 1000 pounds per square inch, whereas the elongation is that recorded on a 4" gauge length, unless otherwise stated. Also included in Table III are the grain sizes for the annealed alloys, measurements being made by the linear intercept method, a minimum of 500 grains being counted per specimen in the x and y directions in the plane of the foil.

Three grades of methanol were used in studying the effect of methanol purity on the cracking characteristics, a purified grade, a reagent grade and a GC-Spectrophotometric quality*. The purified grade was the lowest purity of the three and contained 0.14% H₂O. The spectrophotometric methanol assayed 99.9+ % and contained 0.008% H₂O. The reagent grade alcohol contained 0.02% H₂O (Cat. No. 9070) with an assay of 99.9% and it is the alcohol normally used in the laboratory for the preparation of the testing solutions. The three methanols were analyzed by gas chromatography for the presence of impurities. Separations were made on each of two columns, namely, a 6 ft. x 1/4 in. column packed with 10% Carbowax 20M-TPA on teflon at 75°F and a 4 ft. x 1/4 in. column with Porapak Q beads at 115°F; the major impurity detected was water which varied as indicated. Uniform traces of formaldehyde were present in all samples. Formic acid was not detected. A higher boiling component was also present, but in amounts too small to be positively distinguished from base-line noise.

* J. T. Baker Chemical Co., Phillipsburg, New Jersey, Cat. No's. 9076, 9070 and P707, respectively.

The details of equipment, apparatus and testing procedures were reviewed in detail in Semi-Annual Progress Report No. 4. In the latest period, a fractographic examination of failed specimens of titanium has been conducted using a Jeolco JSM Type 2 Scanning electron microscope.

EXPERIMENTAL RESULTS AND DISCUSSION

Effect of Halide Concentration and Methanol Purity on Cracking Susceptibility

Subsequent to the results reported in our recent publication¹⁾ and in Progress Report No. 5, the specimens of 99.5 Ti were tensile tested, after having been exposed to methanolic solutions containing 10^{-6} N HCl for 5000 hours under 75% Y.S. with no failure. The results from such tests are shown in Table IV. It can be seen that the strength values show no deterioration, and it may be reasoned that the lower elongation values in two instances result from inaccuracies in the testing procedure of these single specimens, particularly as the low values bear no systematic relationship to the water content. These results, therefore, further support the contention that methanolic solutions containing 10^{-6} N HCl behave similarly to solutions of pure methanol in that they do not promote failure in stressed titanium specimens. A minimum chloride concentration in the range 10^{-5} to somewhat more than 10^{-6} N HCl is required before such solutions can promote susceptibility.

Work on the effect of low halide concentrations on the cracking susceptibility of 99.5 Ti has been extended to NaBr and NaI, and the results are shown in Figures 1 and 2. Figure 1 shows the time to failure versus volume percentage water in methanol for methanolic solutions containing

1N and 10^{-2} N NaBr. Also shown is the time to failure curve for specimens in methanolic solutions containing 10^{-2} N NaCl. Figure 2 shows the electrode potential values recorded in solutions containing varying concentrations of NaBr and NaI. Similarly to solutions containing NaCl, the NaBr containing solutions show a typical minimum with failure times first decreasing then increasing sharply with increasing amounts of water. Also, as the NaBr concentration is reduced, the times to failure are correspondingly increased. For bromide concentrations less than 10^{-2} N NaBr, the specimens consistently broke in contact with the polyethylene bottle holding the solution around the specimen, producing widely scattered results. At the present time, the reason for the occurrence of such contact breaks is not known. However, on measuring the electrode potentials of specimens in solutions containing lower concentrations of NaBr, Figure 2, it can be seen that the results are very similar to those in solutions containing low concentrations of HCl⁽¹⁾. The electrode potentials in solutions containing no NaBr are also shown. The results for solutions containing 1N, 10^{-2} N and 10^{-3} N NaBr are very similar to those observed for titanium alloys which fail in methanol-water-HCl environments; i.e., low values of electrode potentials at the lowest water concentrations followed by a sharp increase to more noble values as water is added. However, the curves for 10^{-4} N NaBr and no added NaBr are characterized by no sharp increases in slope except at much higher water contents and more noble values at lower water contents. Taking into consideration the results for HCl⁽¹⁾ it would seem reasonable to assume that a limit will also exist for the concentration of NaBr in methanolic solutions below which no failures will occur and possibly this limit may be higher than the limit for

HCl. This would then help collaborate a film pitting mechanism of crack initiation as bromide ions are weaker pitting agents than chloride ions.

In methanolic solutions containing varying concentrations of NaI no failures of 99.5 Ti were recorded, and Table IV shows the tensile properties of specimens exposed to such solutions under 75% Y.S. for varying times. It is evident that no deterioration has occurred in the tensile properties indicating that no corrosive attack of the metal has taken place. The electrode potential values in solutions containing 3.5N NaI and 10^{-5} N NaI are shown in Figure 2 and are characterized by no sharp increases in potential as the water content is increased, and consistently show values more noble than -100mV (S.C.E.).

Methanolic solutions containing iodide ions were also unable to crack a few samples of Ti-6Al-4V alloy exposed at 75% yield strength for times up to 1000 hours. Electrode potential measurements also indicated that cracking would not be expected. However, a Ti-6Al-4V alloy previously reported⁽²⁾ did crack in methanol with the very lowest water contents and 10^{-2} N NaI added. Electrode potential measurements gave more of an indication of cracking possibilities than for the alloy recently studied. It would appear that the Ti-6Al-4V alloy is on the very edge of susceptibility to cracking in methanol containing iodide ions.

Generally, therefore, for solutions containing NaBr and NaI, as well as for solutions containing HCl, the values of electrode potential give a strong indication as to whether or not failure will occur; i.e., whether or not the specimen potential is in the critical range for crack initiation. There is also a possibility that the aggressiveness of the

solutions to promoting cracking and the progressively weaker film pitting capabilities of the chloride, bromide and iodide ions are intimately related.

As part of the continuing investigation into the effect of impurities in solution on the cracking characteristics, three different grades of alcohol were used in making up the testing solutions, as explained in the section, "Materials and Procedures". Figure 3 shows the results obtained for Ti-6Al-4V alloy in solutions containing 10^{-2} N NaCl, as a function of water content. Apparently in the spectrophotometric purity methanolic solutions, slightly less water is necessary to inhibit the cracking process, and the times to failure at the minimum are slightly longer, otherwise there is not much difference among the three methanols just as the gas chromatography analysis indicated. On attempting equivalent experiments using Ti-13V-11Cr-3Al, an unusually large amount of scatter was recorded in the times to failure, particularly in the solutions made with the lower purity methanol. Again, however, the trend seemed to be followed that the higher the purity of the methanol, the less water is needed to prevent failure.

Effect of Solution Composition on S.C.C. Behavior of Ti-6Al-4V Under Applied Anodic and Cathodic Polarization Currents

Traditionally in the field of S.C.C., the prevention of failure by the application of a cathodic current has been thought to invalidate the existence of a hydrogen embrittlement mechanism. In recent times, however, Powell and Scully⁽³⁾ have opposed this argument by reasoning that, at least

in the S.C.C. of titanium alloys, cathodic currents may result in the formation of films which act as an efficient barrier against the ingress of hydrogen into the metal. In the light of this most recent work, it was decided that a study of the effect of applied currents on the S.C.C. behavior of a commercial titanium alloy might be worthy of a detailed examination. The commercial titanium alloy containing nominally 6% Al and 4% V was used, varying such solution parameters as pH, chloride concentration and water content. The solution pH was most conveniently altered when HCl instead of NaCl was used as a means of introducing the necessary chloride ions⁽¹⁾.

Figure 4 shows the results for solutions containing $10^{-2}N$ HCl as a function of water content. The water carry over from the HCl is 0.05%, so the minimum limit for the water content was 0.06% (0.01% from the methanol). This work showed that cracking did indeed occur under cathodic currents, the cathodic current density required for the prevention of cracking being a direct function of the water content. Thus the lower the water content of the solution, the higher is the cathodic current density needed to prevent failure. However, on the anodic side of the current density abscissa, the higher the water content, the greater is the susceptibility to failure.

Under conditions of zero applied current, the amount of water needed for inhibition of cracking is approximately 0.35%, so to see whether the times to failure would be progressively decreased as the water content was increased, the behavior under an anodic current density of 4 mA/in^2 was investigated as a function of water content. Figure 5 shows the results obtained together with equivalent results under zero applied current conditions, plotting time

to failure versus volume percentage water in methanol. Under anodic polarization the range of failure can be extended to solutions containing 100% H_2O , and it can be readily seen that the time to failure is not a simple function of water content. Visual and microscopical examination of failed specimens revealed the initiation of a pitting mechanism at approximately 20-25% H_2O , and indeed the specimen failed at 40% H_2O had about 10 perforations averaging about 1mm diameter. As the water content is further increased, the pitting becomes increasingly more severe until at 90% H_2O failed specimens are found to contain large edge pits which have consumed approximately half the foil width. In solutions containing 100% H_2O , although the pitting was severe, it was not as severe as in the water solutions containing some methanol. In solutions containing less than approximately 25% H_2O , the density of cracking seemed to be a function of the water content, increasing as the water content increased. However, when macroscopic pitting and perforation occurred, the density of cracking along the gauge length decrease sharply although in the vicinity of the fracture there still remained a high crack density.

The behavior under the effect of applied currents in methanolic solutions containing NaCl contrasted strongly with that in solutions containing HCl. As can be seen in Figure 6, the effect of anodic currents decreased the times to failure. However, on the cathodic side, even in solutions containing only 0.01% H_2O , breaks were only recorded at -0.2 mA/in^2 and to promote these breaks, the chloride content had to be increased to 0.1N NaCl. This is close to the maximum solubility limit for NaCl in methanol, approximately 0.15N NaCl.

Although it has been shown that a sufficient cathodic current density will prevent failure in foil specimens of Ti-6Al-4V stressed to 75% Y.S. in methanolic solutions, it is also clear that the pH and water contents of the solution must also be taken into consideration. pH measurements of solutions containing NaCl varied in the range 5.5 to 6.0 depending on water content. The pH of the water used was 6.0. For solutions containing HCl, however, the pH was as low as 0.1 in solutions containing 0.06% H₂O increasing to 0.3 in solutions containing 0.5% H₂O.

Taking into account the work by Scully^(3,4), it would seem reasonable to suggest the following as a possible explanation for the results in Figures 4 and 6, assuming in this instance that hydrogen is a necessary activating agent for the cracking mechanism. In the NaCl containing, slightly acid solutions, the application of a cathodic current sharply increases the ratio $\text{OH}^-:\text{Cl}^-$ at the crack tip resulting in a stable barrier film which restricts the entry of hydrogen into the metal. Evidently, in solutions where this ratio is initially lower; i.e., 0.1N NaCl cf 10^{-2} N NaCl, cracking is still possible under very small cathodic current densities but only then when the water content is very low. However, in the very low pH solutions containing 10^{-2} N HCl, the film is no longer stable and it is possible for hydrogen to enter the metal. Increasing the percentage of H₂O increases both the $\text{OH}^-:\text{Cl}^-$ ratio and the pH although the former effect probably exerts the biggest influence in requiring a smaller cathodic current for prevention of cracking. In solutions containing more than 0.25% H₂O, even though the pH is only 0.3, the $\text{OH}^-:\text{Cl}^-$ ratio is sufficiently high to maintain an effective film barrier. The complete protection afforded by the surface

film to specimens cathodically polarized in which no failure was recorded in 500 hours, was demonstrated by the mechanical testing of such specimens. In all cases, the tensile properties were unchanged from their original values. The necessity for a higher preventative cathodic current in the low pH solutions containing less than 0.25% H_2O lends support to the role of hydrogen which would be more apt to be evolved under such acid conditions.

The acceleration of failure produced by anodic polarization of the stress specimens illustrates the presence of a dissolution mechanism which will be discussed more fully in a later section dealing with the effects of pre-corrosion on the cracking susceptibility.

An interesting feature of the results shown in Figure 5 was the failure of specimens in solutions containing a minimal amount of methanol and also in aqueous solutions containing $10^{-2}N$ HCl. A metallographic examination of specimens failed in the latter solutions revealed an absence of cracking along the gauge length. However, adjacent to the fracture edge and at the leading edge of the pits cracking was indeed visible, particularly so at the fracture surface. It would, therefore, appear that under the right conditions cracking of Ti-6Al-4V is also possible in aqueous solutions, the nature of the pits being either to act as stress concentrators or to promote a reactive environment within the pits. Scully^(4,5) has also reported cracking of un-notched specimens of Ti-5Al-2.5Sn in aqueous solutions containing 3% NaCl, but only in a specific range of strain rates.

Effect of Pre-corrosion on the S.C.C. Behavior of 99.5 Ti and Ti-6Al-4V

Previous work in this laboratory has established the susceptibility of titanium and titanium alloys to corrosion in methanolic solutions⁽⁶⁾. The phenomenon has been investigated by exposing foil specimens to the solutions for varying times, followed by tensile testing to determine residual tensile properties. The main points to arise from this work were: 1) ultimately the corrosion reaction results in a complete loss of strength of the metal, the time needed depending on the particular alloy and metallurgical condition, 2) the higher the water content of the solution, the slower is the rate of deterioration of the metal, 3) the embrittling process proceeds without the obvious formation of any corrosion products, and 4) comparing times to failure of specimens loaded to 75% Y.S. with the rates of deterioration under free corrosion shows that factors other than corrosion effects must be operative in the cracking mechanism; e.g., for 99.5 Ti and Ti-6Al-4V in $\text{CH}_3\text{OH} - 10^{-2}\text{N HCl} - 0.09\% \text{H}_2\text{O}$, the times to failure are 3.6 hours and 5.5 hours, respectively, but the exposure times with no load necessary for 50% reduction in elongation are 4.25 hours and 240 hours, respectively⁽⁷⁾.

Recently Cocks et al.⁽⁸⁾ have attempted to separate the effects of corrosion and stress for Ti-6Al-4V in methanolic solutions containing bromine. The method they used was to expose the alloy to the solution for varying times prior to loading, and plotting the time to failure after pre-corrosion versus the pre-corrosion time.

Figure 7 shows the results obtained in this laboratory for specimens of 99.5 Ti and Ti-6Al-4V as a function of water content. The ordinate and abscissa have been normalized by dividing by the normal failure time in each

solution, with the load and solution added simultaneously. If pre-corrosion has no effect on the time to failure, the results would be expected to lie along the broken horizontal line, whereas if the rate of deterioration due to corrosion proceeds independently of the applied stress, the results would be expected to lie along the broken line with a gradient of one. Thus, it should be possible to differentiate between a S.C.C. mechanism and a purely corrosion mechanism.

The results shown in Figure 7 strongly suggest that in the case of 99.5 Ti in the annealed condition, failure results, at least in the low water content solution, from deterioration produced solely by the corrosion reaction. The interpretation of the results produced by the higher water content solutions would seem to be concerned with the inhibiting effect of water on the corrosion reaction. In this instance, the less rapid rate of deterioration would be a direct consequence of the lower reaction kinetics of the corrosion process. It is also likely that the applied stress might accelerate the corrosion reaction to some extent by causing film breakdown by the stress concentration produced at the crack tip.

In the case of the Ti-6Al-4V alloy, the rate of deterioration is far less and it might appear from the shape of the curves that they eventually reach a limit beyond which subsequent corrosion damage does not occur. This would correspond to the situation recorded by Cocks *et al.*⁽⁸⁾ for Ti-6Al-4V in methanol containing 0.8 volume percent of bromine. However, it should be noted that they only plotted results for specimens pre-corroded for times equivalent to three times the normal failure time, and it seems extremely unlikely that for more prolonged times no further deterioration

would occur. In the present work, normalized time to failure values of 0.16 and 0.48 were obtained for normalized pre-corrosion times of 56.2 and 69.0 (not plotted), for Ti-6Al-4V in solutions containing 0.08% and 0.20% H_2O respectively. Thus, there is a continual, though small, effect of pre-corrosion on the failure times as the period of exposure is further increased from that shown in Figure 7.

The case for an exclusive stress corrosion mechanism is never quite met as is the case for a strict corrosion mechanism. Except for the one curve with a gradient of one, the other curves would indicate that stress is intimately involved in the cracking mechanism. Further evidence of this will be shown in the next section involving a fractographic examination of the fracture surfaces of specimens failed in methanolic solutions.

Failure of Crystal Bar Titanium in Methanolic Solutions

Annealed specimens of the iodide process titanium were found to be no less susceptible to failure in methanolic solutions than annealed specimens of 99.5 Ti. Figure 8 shows the results obtained in solutions containing $10^{-2}N$ HCl and $10^{-2}N$ NaCl, together with curves for 99.5 Ti in similar chloride containing solutions. However, whereas for the 99.5 Ti there is very little difference whether the solution contains NaCl or HCl, this is definitely not the case for the crystal bar titanium. As can be seen, solutions containing HCl lower the failure times by nearly an order of magnitude compared with solutions containing NaCl, and also the water content needed for inhibition of the cracking process is increased from

0.3% to 0.65%. The mode of failure is intergranular as in the 99.5 Ti, and fractographs of the S.C.C. fracture surface reveal no differences between the two grades of titanium (see later section). At the present time, the reason for the enhanced susceptibility in the HCl containing solutions is not known.

The fact that the annealed crystal bar titanium is just as susceptible to failure in methanolic solutions as 99.5 Ti and 99.0 Ti⁽⁹⁾ strongly suggests that segregation of trace impurities to the grain boundaries is responsible for the selective intergranular attack.

S.C.C. of Rod Specimens

Figure 9 shows the results obtained with the rod specimens of Ti-6Al-4V together with similar results obtained with foil specimens of the same nominal composition. It is readily seen that the rod specimens are equally susceptible to failure in methanolic solutions, and in fact under the present set of testing conditions are even more so. Also, the shape of the time to failure curve is similar in that a small amount of water accelerates the cracking process but eventually complete protection is obtained at approximately 0.7% H₂O.

The shape of the load-time curve was characteristic for all the specimens tested in that after the initial load relaxation, the load remained constant until approximately the last 10 minutes when it decreased sharply before sudden failure. On examination under a power of 20X, the only cracks visible were those near the fracture surface which had yawned due to the deformation accompanying the propagation of the main crack.

The fracture surface topography for any one specimen was characterized by three regions; an extremely rough crack initiation region, a macroscopically flat fast crack propagation area, and a tear lip usually inclined at approximately 45° to the tensile axis. These regions were macroscopically very similar in appearance to those recorded by Williams⁽¹⁰⁾ for the failure of pre-fatigue cracked specimens of Ti-6Al-4V in 3 1/2% NaCl aqueous solutions.

A limited number of rod specimens of the alloy Ti-5Al-5Sn-5Zr were also tested in methanolic solutions and time to failure values of the same order of magnitude as those shown in Figure 9 were recorded. Due to the limited number of specimens, it was not possible to define the shape of the curve of time to failure versus water content. However, there is no reason to believe that it would be markedly different to those shown in Figure 9. The load-time curves were similar in shape to those for Ti-6Al-4V, although during the crack initiation period there was a continual, though small, relaxation in the load, probably due to continual relaxation of the specimen. The fracture surfaces were rough with no macroscopically flat portion of the magnitude found on fractured specimens of Ti-6Al-4V. Also, the only subsidiary cracking occurred in the deformed region adjacent to the main fracture surface.

Fractographic Examination of Rod and Foil Specimens

Facilities were recently made available for the use of a scanning electron microscope, and a preliminary fractographic examination was made of representative specimens of both foil and rod specimens, which had been tested in methanolic solutions in this laboratory. The corrosion resistant

nature of titanium exposed to the atmosphere and the absence of corrosion products in methanolic solutions, which might otherwise camouflage the fine details of the fracture surface, make this an ideal system to study.

The fractographs are shown in Figures 10 to 14. The fracture surfaces of the alpha alloys: crystal bar titanium, 99.5 Ti, Ti-0.2 Pd and Ti-5Al-5Sn-5Zr are seen to exhibit largely granular facets, indicative of an intergranular cracking mechanism, whereas the fracture surfaces of Ti-6Al-4V and Ti-13V-11Cr-3Al show no evidence of grains, indicating a transgranular mode of failure. In the case of the crystal bar and 99.5 Ti and Ti-0.2 Pd, the grains are smooth sided and show no evidence of pitting or corrosion, Figure 10 (E) and (F), Figure 11 (B) and (C), Figure 14 (C). The markings shown on the sides of the grain in Figure 10 (E) for 99.5 Ti are very similar to those shown by Scully⁽³⁾ for Ti-5Al-2.5Sn, and probably result from glide separation. In the case of Ti-5Al-5Sn-5Zr, areas can be seen in which markings characteristic of a cleavage mode of failure are visible, Figure 13 (C) and (D), suggesting that this alloy is susceptible to both intergranular and transgranular modes of failure. The Ti-13V-11Cr-3Al and Ti-6Al-4V both show evidence of striations indicating a discontinuous mode of transgranular crack propagation, Figure 11 (E) and (F), Figure 12 (B) and (C), although the topography does not seem to be characteristic of the usual markings observed on specimen surfaces failed by cleavage. The surface of the cold rolled 99.5 Ti, Figure 10 (B), has no predominant features, though it is thought significant that it shows no signs of cleavage or discontinuous crack propagation. The rod specimens of Ti-6Al-4V and Ti-5Al-5Sn-5Zr have features much the same as the corresponding foil specimens of the same nominal composition. Thus, in the crack initiation

stages both show evidence of discontinuous propagation, Figures 12 (E) and 13 (F), particularly so in the Ti-5Al-5Sn-5Zr, although the latter shows very little evidence of granular separation. In both alloys the crack propagation stages, Figures 12 (F) and 14 (B) exhibit features bearing no characteristic trade-marks. Overall, the air tensile specimens have a characteristically dimpled surface indicating ductile failure resulting from micro-void coalescence.

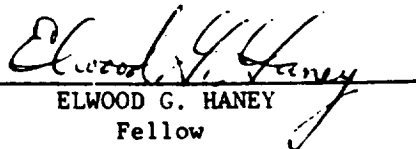
The fractograph shown in Figure 14 (D) is from a sample of the crystal bar titanium exposed in the unstressed condition to $\text{CH}_3\text{OH} - 10^{-2}\text{N HCl} - 0.10\% \text{H}_2\text{O}$, for 64 hours. On removal from the solution, total embrittlement of the metal had occurred, which could be easily broken by a light pressure of the fingers. It is seen to be almost identical with a similar specimen exposed to the same solution under 75% Y.S., Figure 14 (C), although the grains give the appearance of being less tightly bound, as indeed would be expected in a totally embrittled specimen.

The most important points that have arisen from this preliminary study are thought to be the uncorroded nature of the grain surfaces on fracture surfaces of specimens failed by intergranular cracking, and the strong resemblance of features on the fracture surfaces of transgranularly failed specimens to cleavage markings. In both modes of failure, there is no evidence of ductile parting in the form of dimpling, and it is clear that the cracking mechanism is of a brittle nature.

CONCLUSIONS

- 1) In the case of annealed specimens of 99.5 Ti at 75% Y.S. in methanolic solutions containing 10^{-2} N HCl, failure has been shown to occur by a purely intergranular corrosion type mechanism. For the Ti-6Al-4V alloy in similar solutions at 75% Y.S., corrosion mechanisms can co-exist with stress corrosion mechanisms and either may lead to total failure, though the kinetics of the corrosion process are much slower.
- 2) The failure of specimens of Ti-6Al-4V when cathodically polarized in low pH solutions of low water content, but not in similar solutions containing more than 0.25% H₂O or in near neutral solutions of low and higher water contents, lends support to the proposal by Powell and Scully for the formation of a protective film under cathodic polarization conditions.
- 3) Electrode potential measurements have been shown to provide a valuable tool in predicting whether or not failure will occur in solutions containing NaCl, NaBr or NaI.
- 4) The similar failure times and fractography recorded by rod and foil specimens of Ti-6Al-4V provides justification for the comparison of results obtained from foil specimens with those obtained from bulkier specimens.
- 5) The fractographic evidence shows that the failure of titanium and its alloys in methanolic solutions is a brittle process, the surface features of transgranularly failed specimens bearing markings very similar to cleavage markings.

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FUTURE WORK

- 1) The dependence of cracking susceptibility on the cation of the chloride added to the methanol is being studied, and effort in this direction will be continued in the forthcoming period.
- 2) The fractographic study will be continued, in particular, (a) comparison between fracture surfaces of S.C.C. specimens and fracture surfaces of corrosion specimens tensile tested to determine residual tensile properties, (u) examination of foil surfaces exposed to methanolic solutions in the presence and absence of applied stress to determine sites of chemical attack.
- 3) Determination of the roles of α and β titanium in the cracking process by investigating effects of metallurgical variables such as grain size and structure on the cracking mode, in conjunction with optical and scanning electron microscopy.
- 4) A preliminary study has been made of the behavior of foil specimens, containing a tear, in methanolic solutions under a continually increasing stress. An extension of this study will be made, in particular, (a) correlation of initiation and propagation energies determined from areas under load-extension curves during the time required for failure, (b) examination of the fracture surfaces with the scanning electron microscope, (c) the possibility of using solutions other than methanol, in which cracking can only be promoted in "precracked" specimens.
- 5) Pre-corrosion studies of other alloys and other methanol-water-chloride solutions will continue the task of separating corrosion and stress corrosion effects.

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2. E. G. Haney, et al., Semi-Annual Progress Report No. 2, NASA Research Grant NRG-39-008-014. Carnegie-Mellon University, Mellon Institute, Pittsburgh, Pennsylvania 15213.
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10. J. C. Williams, ASM Trans. Quarterly, Vol. 60, 646 (1967).

TABLE I

Chemical Composition, Weight Percent

Alloy	Designation	Al	V	Zr	Sn	Cr	Pd	Fe	O ₂	C	N	H
99.5Ti	Ti-35A							.07	.07	.023	.010	.004
Ti-Pd	Ti-0.2Pd						.20					
5Al-5Sn-5Zr	Ti-5Al-5Sn-5Zr	5.3		5.3	5.1			.05	.10	.025	.011	.006
5Al-5Sn-5Zr (rod)	Ti-5Al-5Sn-5Zr	5.0		5	5.1			.03	.09	.020	.006	.018
6Al-4V	Ti-6Al-4V	6.4	4.0					.08		.020	.008	.013
6Al-4V (rod)	MST-6Al-4V	6.3	4.2					.24	.10	.020	.007	.006
13V-11Cr-3Al	Ti-13V-11Cr-3Al	3.2	13.8			10.6		.21	.12	.040	.030	.013

TABLE II

Chemical Composition, Weight Percent

Titanium Crystal Bar	
% Si - < 0.001	% Ni - < 0.001
% Al - < 0.005	% Mo - < 0.001
% Mg - < 0.001	% Cu - < 0.001
% Mn - < 0.005	% Sn - < 0.010
% Pb - < 0.001	% Zr - < 0.010
% Cr - < 0.001	% O ₂ - 0.040
% Fe - < 0.001	% N ₂ - 0.040

TABLE III

Tensile Properties of Titanium Alloys

Alloy	Condition	Grain Size (microns)	0.2% Offset Yield Strength (KSI)	Ultimate Tensile Strength (KSI)	Elongation % in 4"
Crystal Bar Ti	Annealed 1 hr. at 1295°F	9	17.6	35.2	40.5 (in 2")
99.5Ti	C. R. [*]	---	103.6	127.2	6.9
99.5Ti	Annealed 1 hr. at 1300°F	15	34.9	47.7	32.5 (in 2")
99.5Ti	Annealed 1/2 hr. at 1495°F	50	31.4	41.8	24.5 (in 2")
Ti-0.2Pd	C. R. [*] and A [†]	5.5	58.8	72.9	23.0
5Al-5Sn-5Zr	C. R. [*] and partially A [†]	24	138.7	156.4	3.9
5Al-5Sn-5Zr (rod)	Annealed 1 hr. at 1600°F	---	121.2	129.8	22.8 (in 1.5")
6Al-4V	C. R. [*] and A [†]	~5	116.3	148.9	9.1
6Al-4V (rod)	Stress Relieved 2 hrs. at 1110°F	---	149	152.5	12.5 (in 1.5")
13V-11Cr-3Al	C. R. [*] and A [†]	16	134.6	135.1	25.9

^{*} Cold Rolled[†] Annealed

TABLE IV

Tensile Properties of 99.5Ti stressed to 75% Y.S.
After Exposure to Methanolic Solutions for Indicated
Time Without Failure

Solution	Exposure Time (hr.)	0.2% Y.S. (KSI)	U.T.S. (KSI)	El. %
10^{-6} N HCl + 0.05% H_2O	5000	38.9	47.6	34.8
10^{-6} N HCl + 0.08% H_2O	5000	38.3	47.0	13.0
10^{-6} N HCl + 0.10% H_2O	5000	37.1	47.0	32.6
10^{-6} N HCl + 0.15% H_2O	3100	38.9	47.6	12.5
10^{-2} N NaI + 0.10% H_2O	1000	37.7	47.6	29.5
3.5N NaI + 0.10% H_2O	356	35.4	47.5	32.0
3.5N NaI + 0.03% H_2O	1075	36.0	47.6	34.0
ORIGINAL PROPERTIES		34.9	47.7	32.5

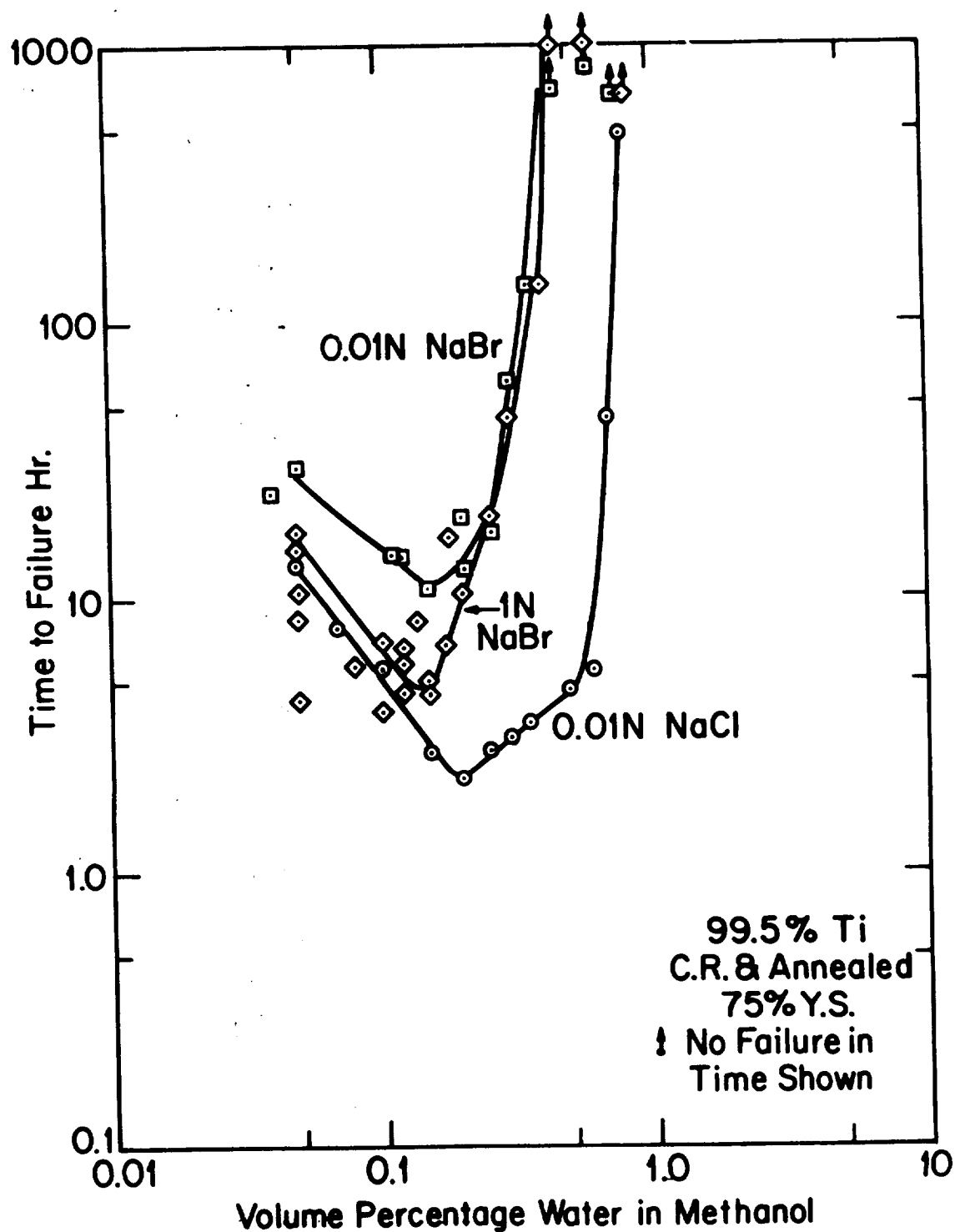


FIGURE 1. Effect of NaBr, NaCl and water content on time to failure.

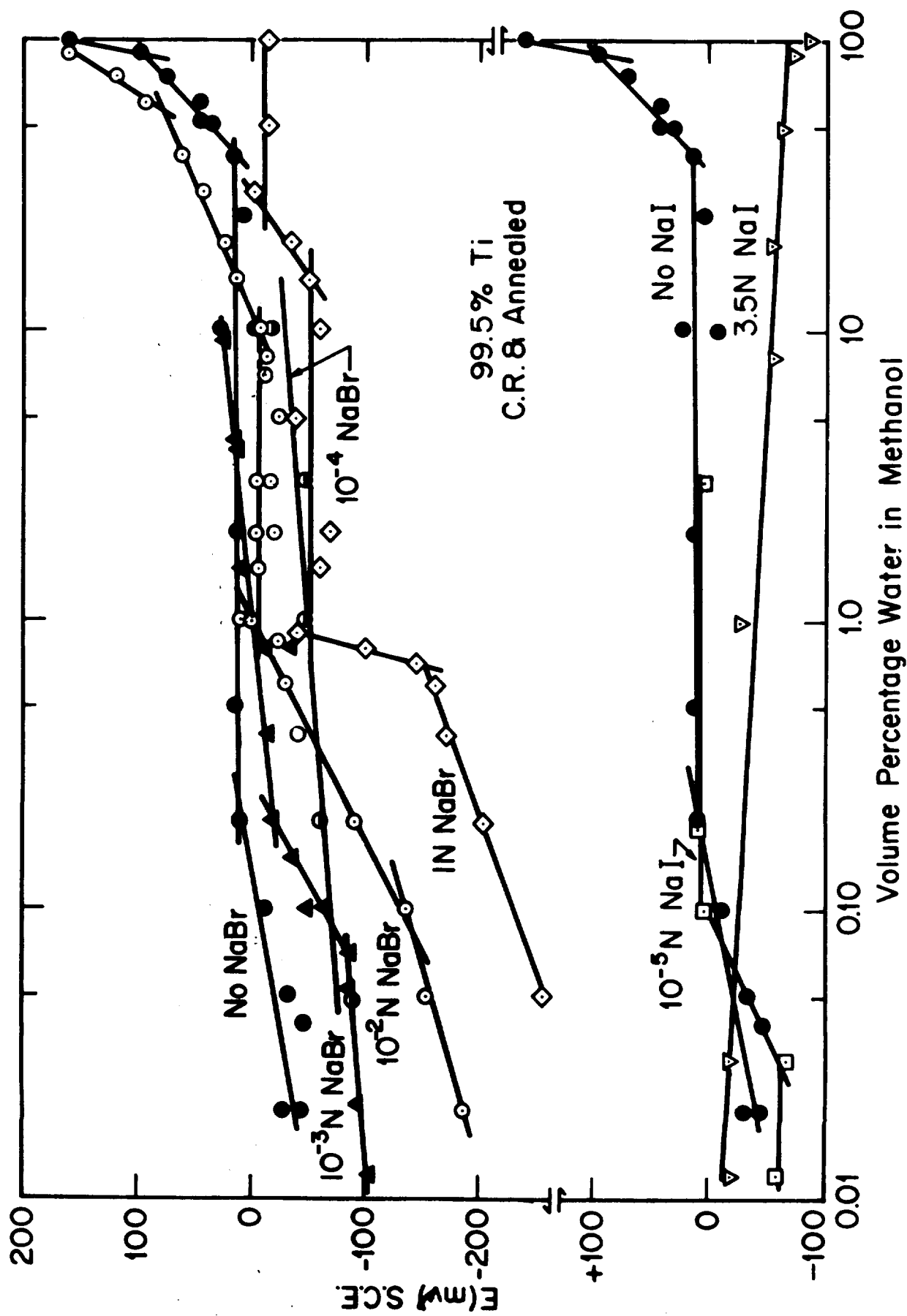


FIGURE 2. One hour electrode potential values as a function of NaBr, NaI and water content.

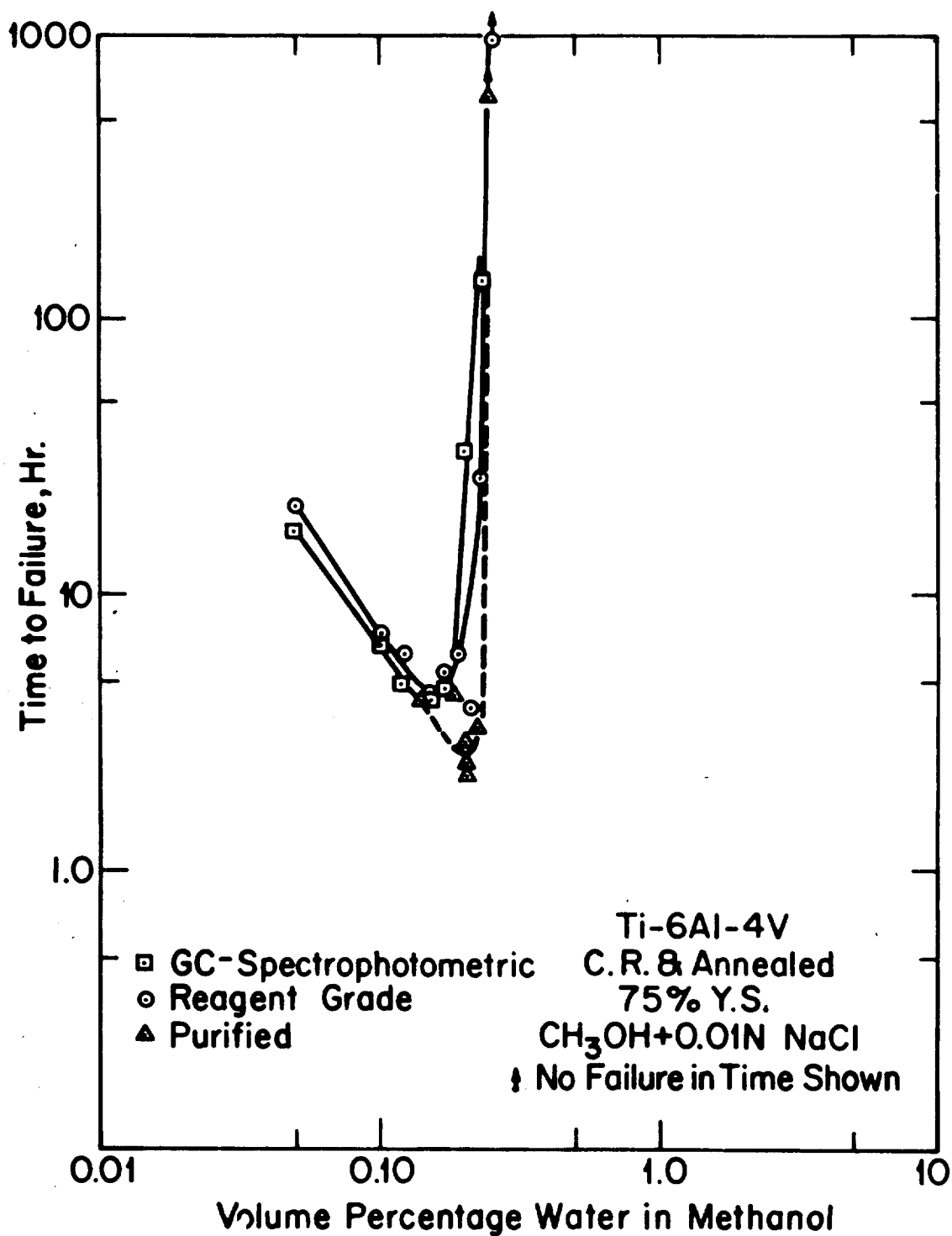


FIGURE 3. Effect of methanol purity on time to failure.

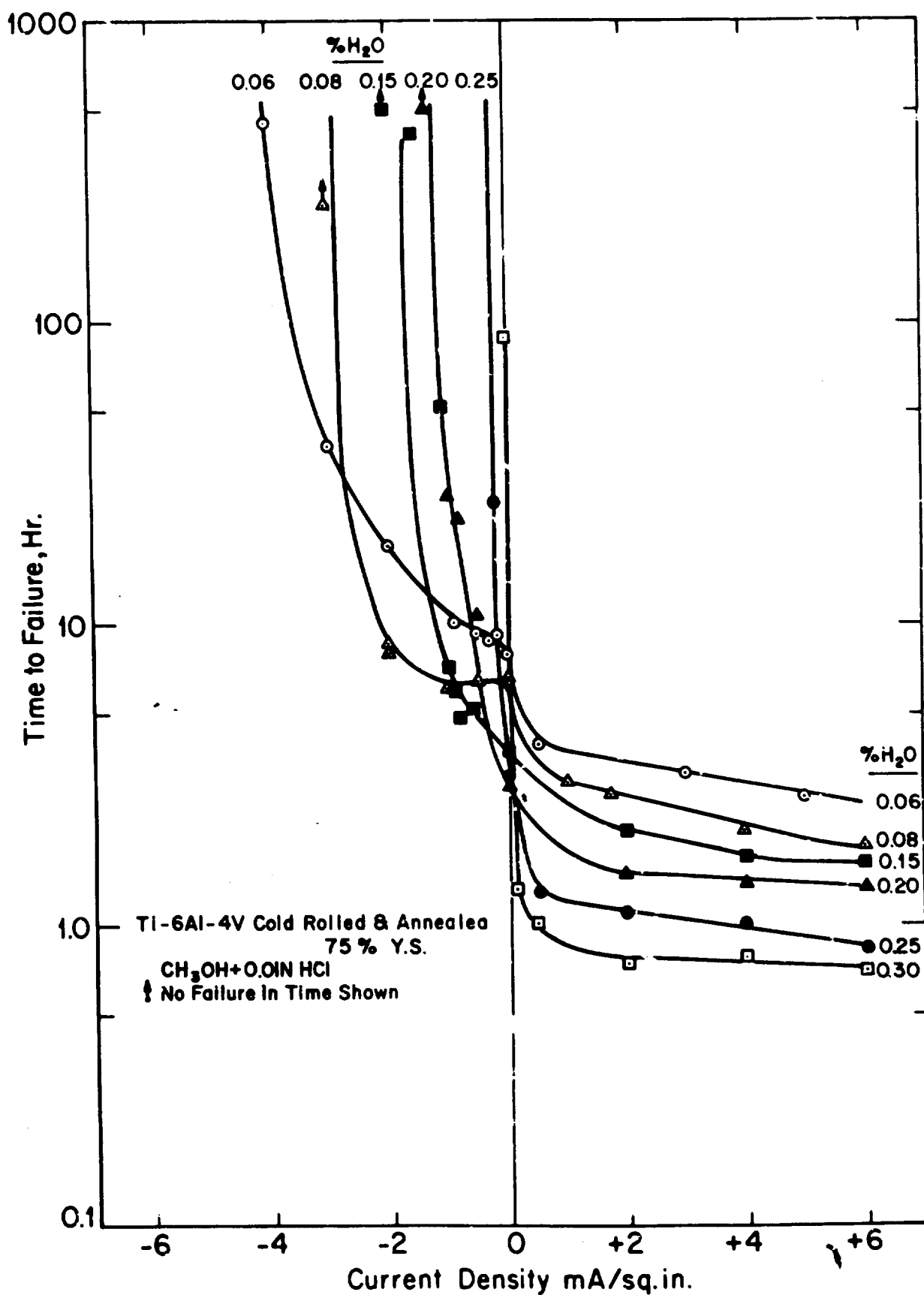


FIGURE 4. Effect of anodic and cathodic polarization on time to failure.

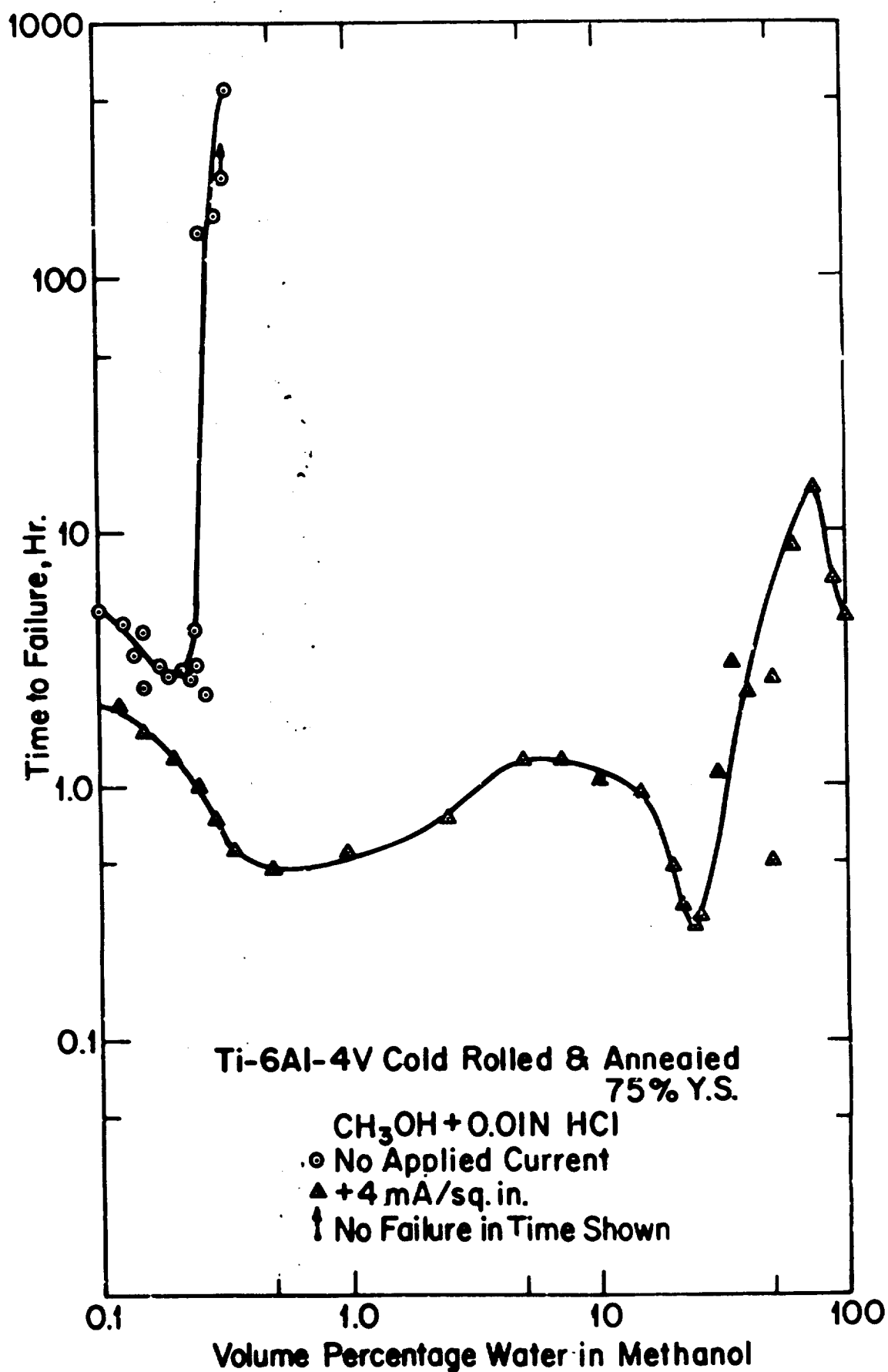


FIGURE 5. Effect of water content on time to failure under anodic polarization.

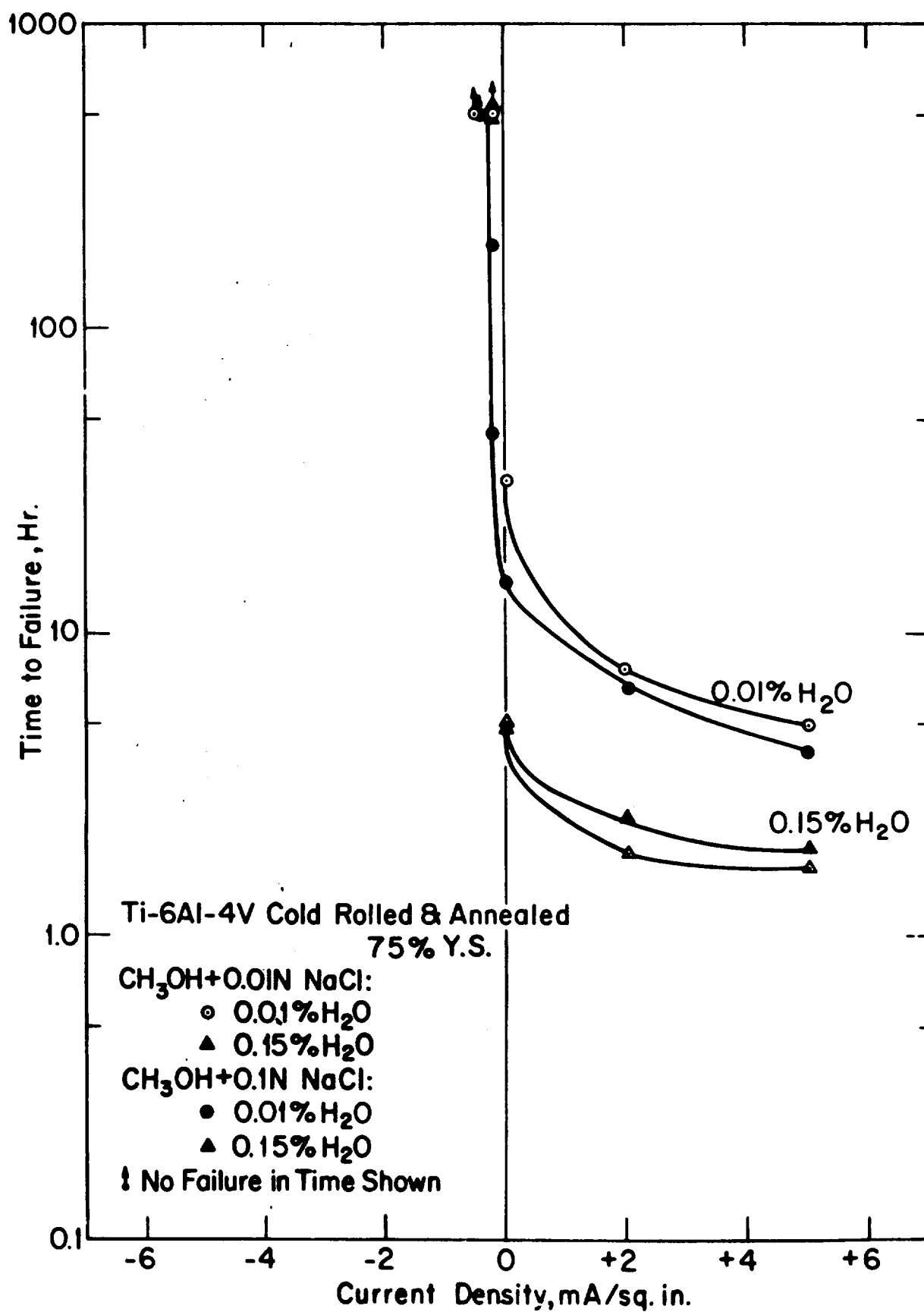


FIGURE 1. Effect of anodic and cathodic polarization on time to failure.

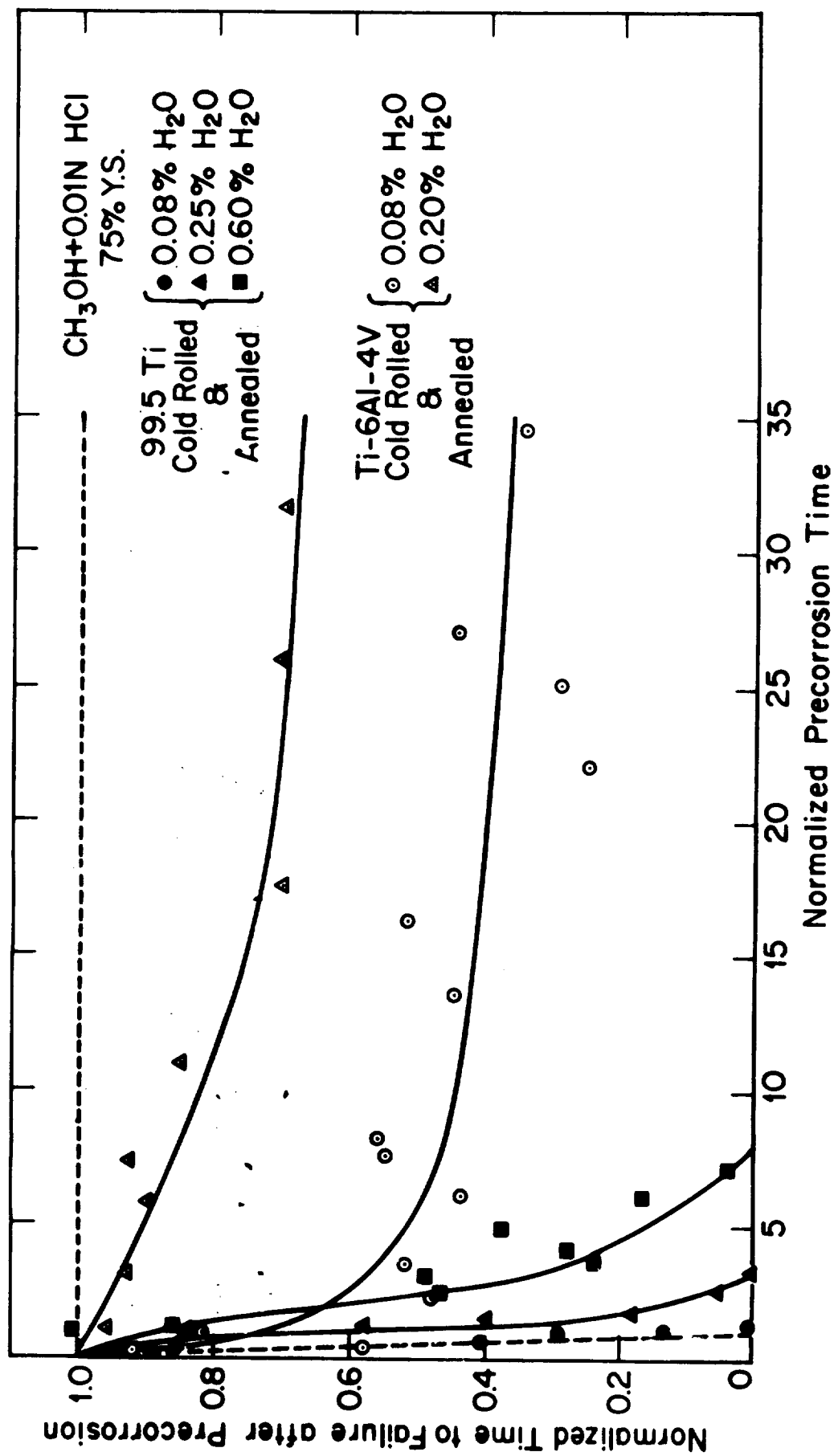


FIGURE 7. Effect of precorrosion on time to failure.

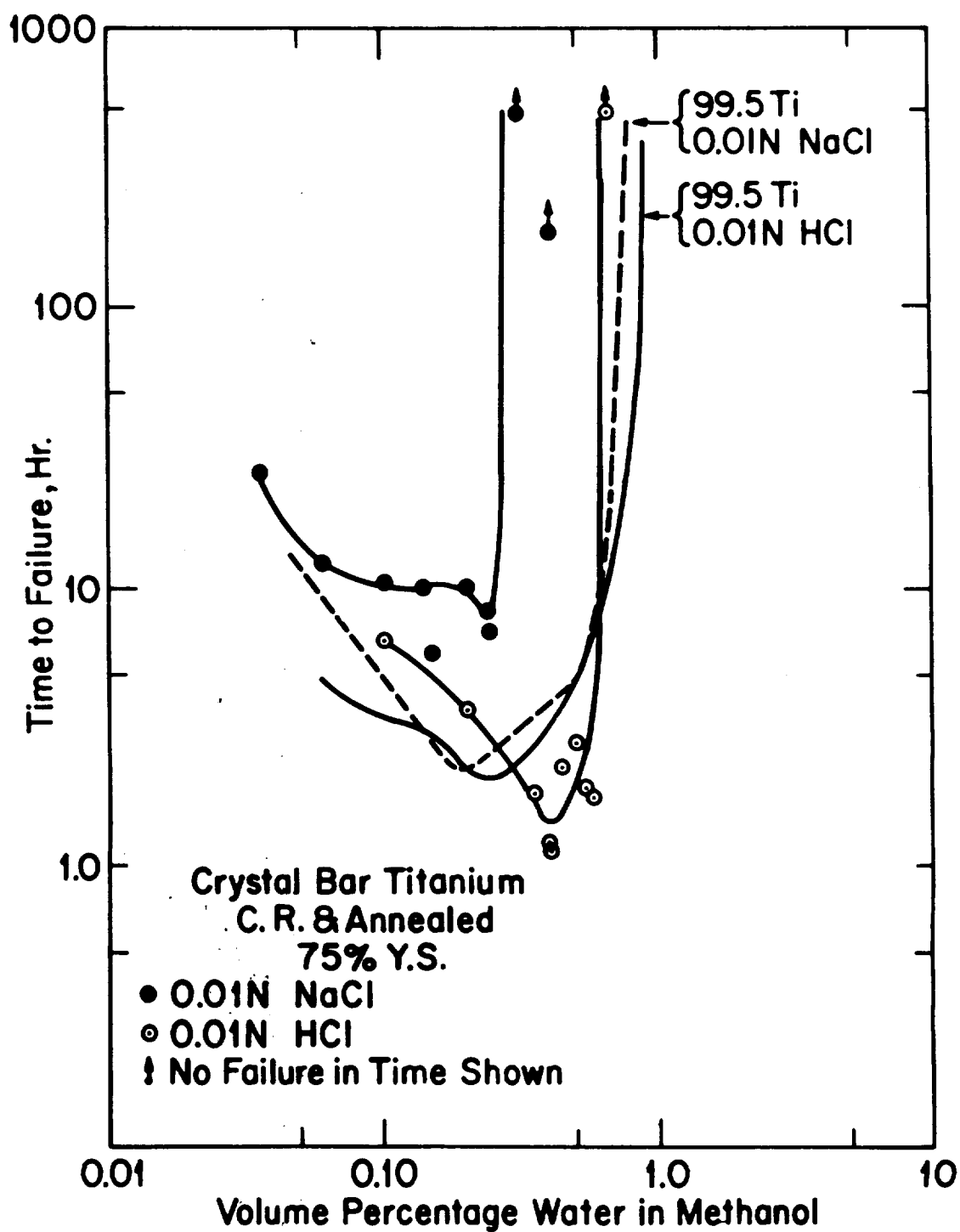


FIGURE 3. Effect of titanium purity and water content on time to failure.

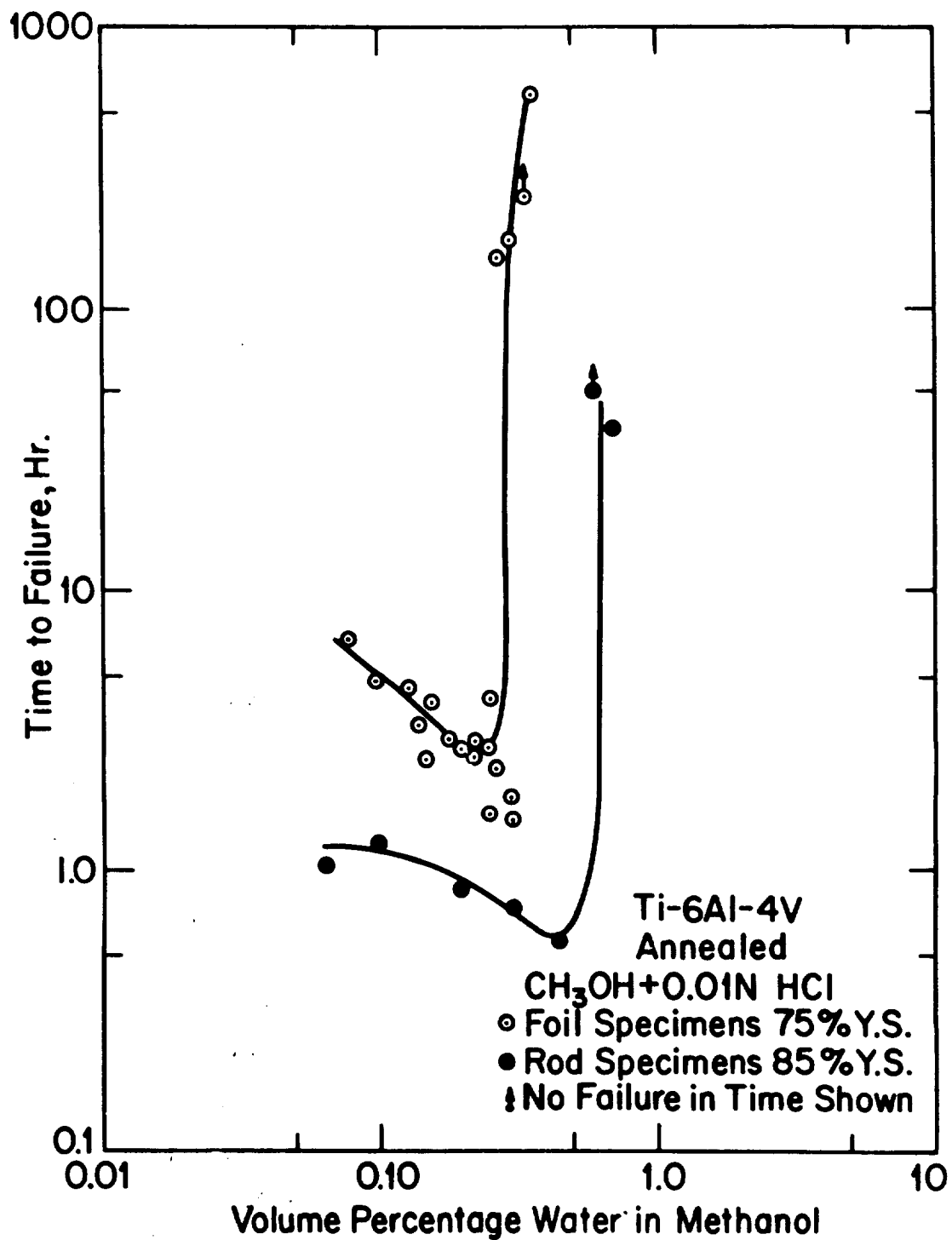
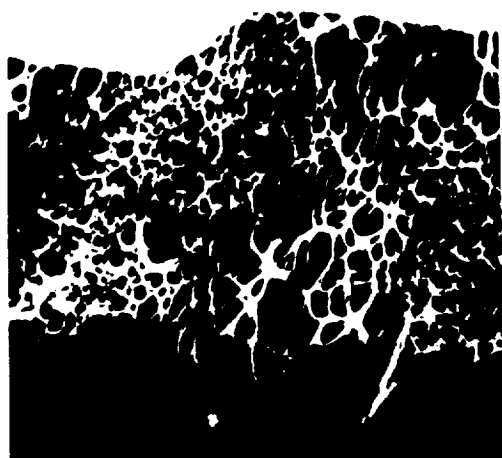
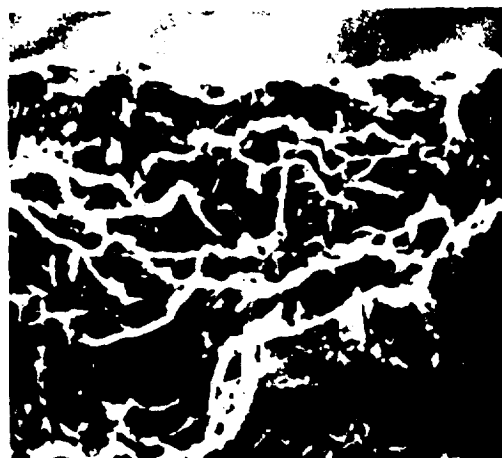


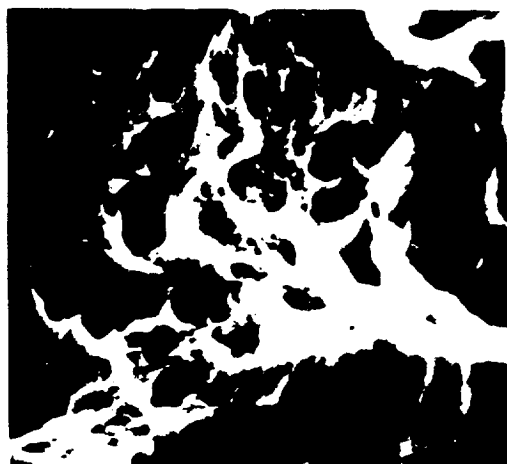
FIGURE 9. Effect of specimen form and water content on time to failure.



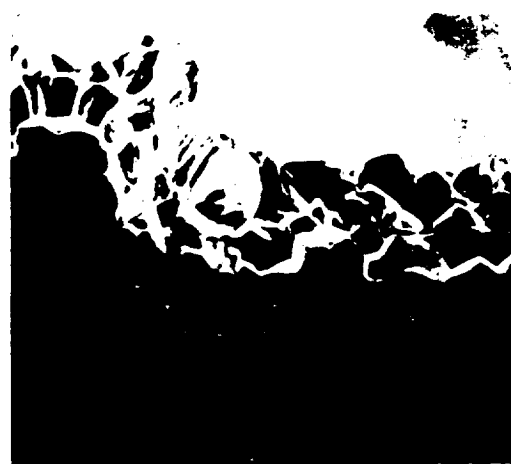
(A) X770



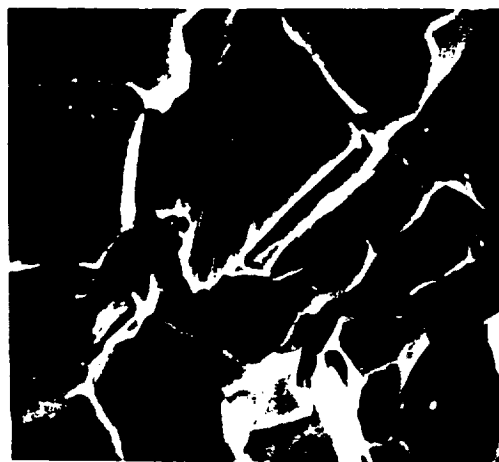
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(C) X2310



(D) X230

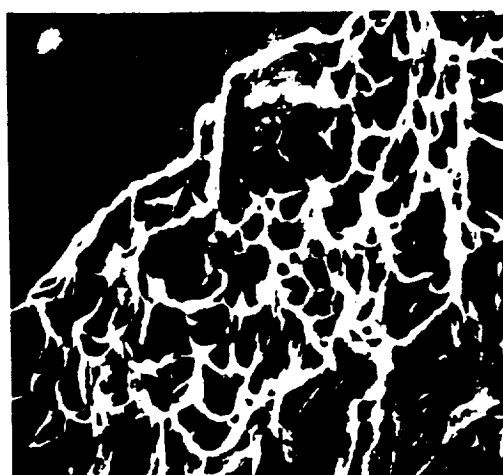


(E) X770



(F) X770

FIGURE 10. Air Tensile, and S.C.C. Specimens of 99.51% Foil in Methanolic Solutions Containing 0.01N H_2O_2 , Stressed at 75% S.S.: (A) Air Tensile, Cold Rolled. (B) S.C.C., Cold Rolled, 0.17% H_2O . (C) Air Tensile, Annealed 1 hr. at 1300°F. (D) & (E) S.C.C., Annealed 1 hr. at 1300°F, 0.09% H_2O and 0.60% H_2O respectively. (F) S.C.C., Annealed 1 1/2 hr. at 1495°F, 0.065% H_2O .



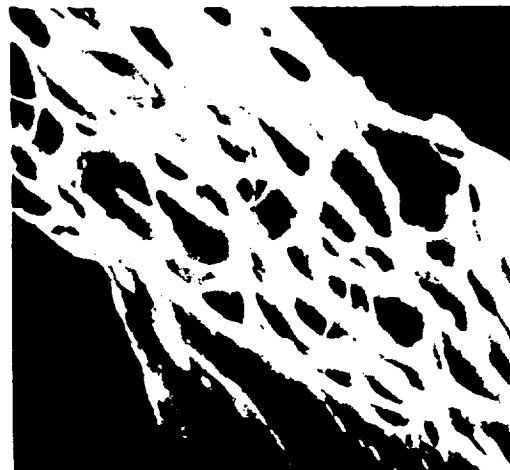
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(B) X1920



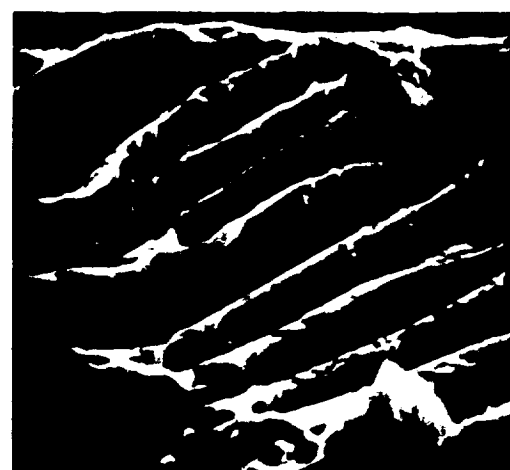
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(D) X2000



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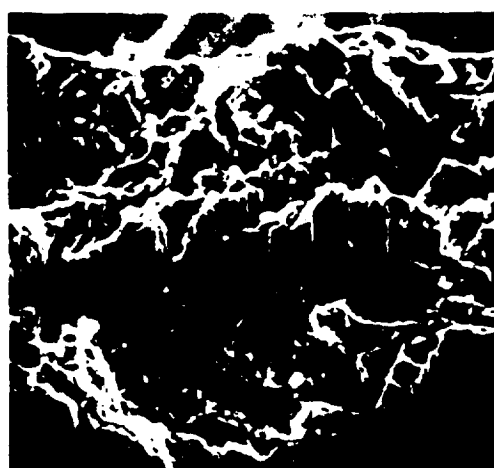


(F) X4240

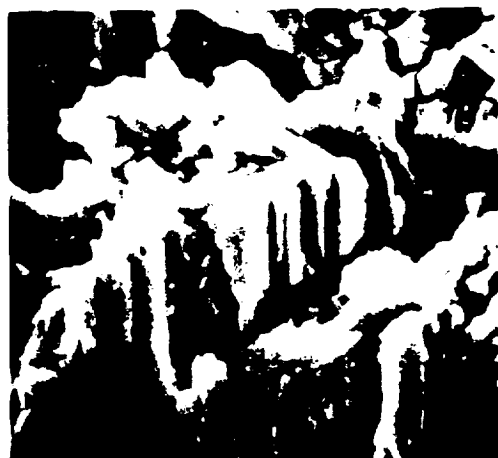
FIGURE 1. Air Tensile, and S.C.C. Specimens of Ti-0.2Pd and Ti-13V-11Cr-3Al Foil in Methanolic Solutions Containing 0.01N HCl, Stressed at 75% Y.S.: (A) Air Tensile, Ti-0.2Pd. (B) & (C) S.C.C., Ti-0.2Pd, 0.70% H₂O. (D) Air Tensile, Ti-13V-11Cr-3Al. (E) & (F) S.C.C., Ti-13V-11Cr-3Al, 0.40% H₂O.



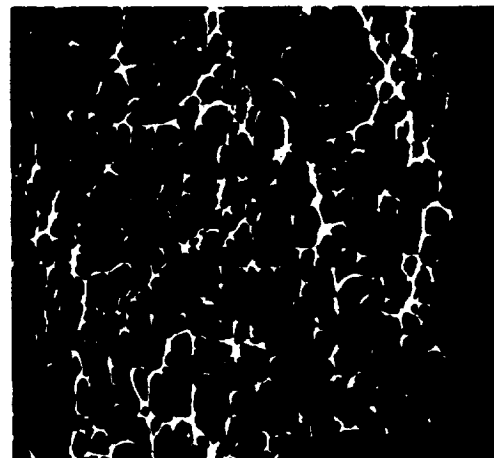
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(B) X540



(C) X2310



(D) X1540

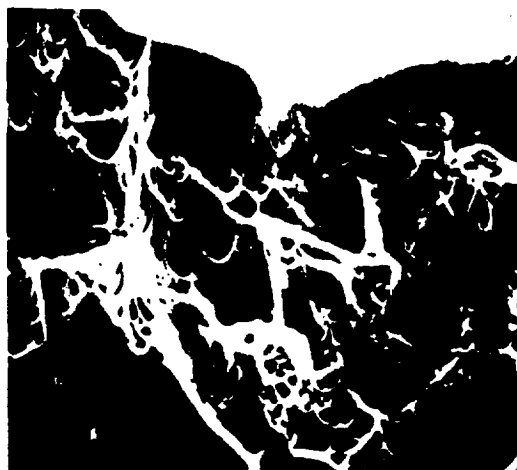


(E) X2310

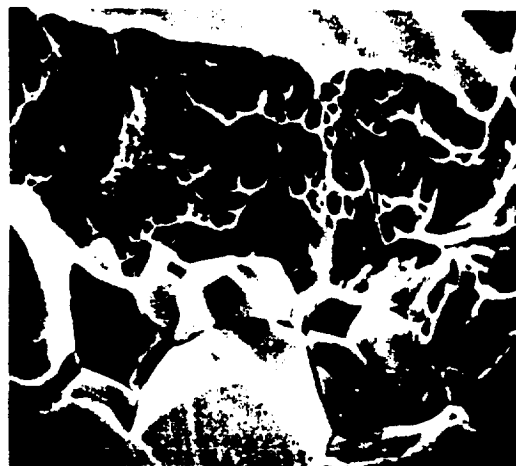


(F) X7700

FIGURE 12. Air Tensile, and S.C.C. Specimens of Ti-6Al-4V Foil and Rod in Methanolic Solutions Containing 0.01N HCl, Stressed to 75% Y.S. and 85% Y.S. respectively: (A) Air Tensile, Foil. (B) & (C) S.C.C., Foil, 0.22% H₂O. (D) Air Tensile, Rod. (E) S.C.C., Rod, 0.065% H₂O, Crack Initiation. (F) S.C.C., Rod, 0.065% H₂O, Crack Propagation.



(A) X770



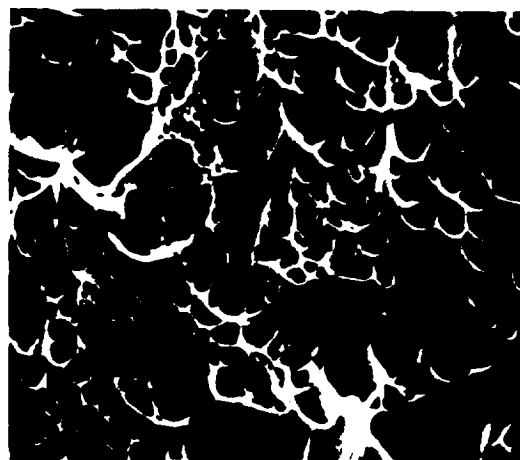
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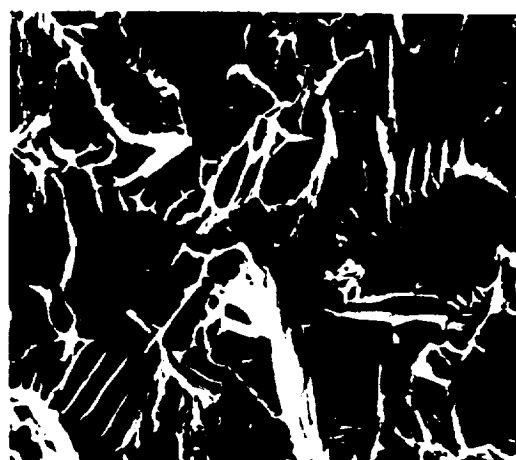
(C) X1540



(D) X5000



(E) X770



(F) X460

FIGURE 13. Air tensile and S.C.C. Specimens of Ti-5Al-5Sn-5Zr Foil and Rod in Methanolic Solutions Containing 0.01N HCl, Stressed to 75% Y.S. and 85% Y.S. respectively. (A) Air Tensile, Foil. (B) S.C.C., Foil, 0.06% H₂O. (C) S.C.C., Foil, 0.30% H₂O. (D) S.C.C., Foil, 0.06% H₂O. (E) Air Tensile, Rod. (F) S.C.C., Rod, 0.19% H₂O, Crack Initiation.

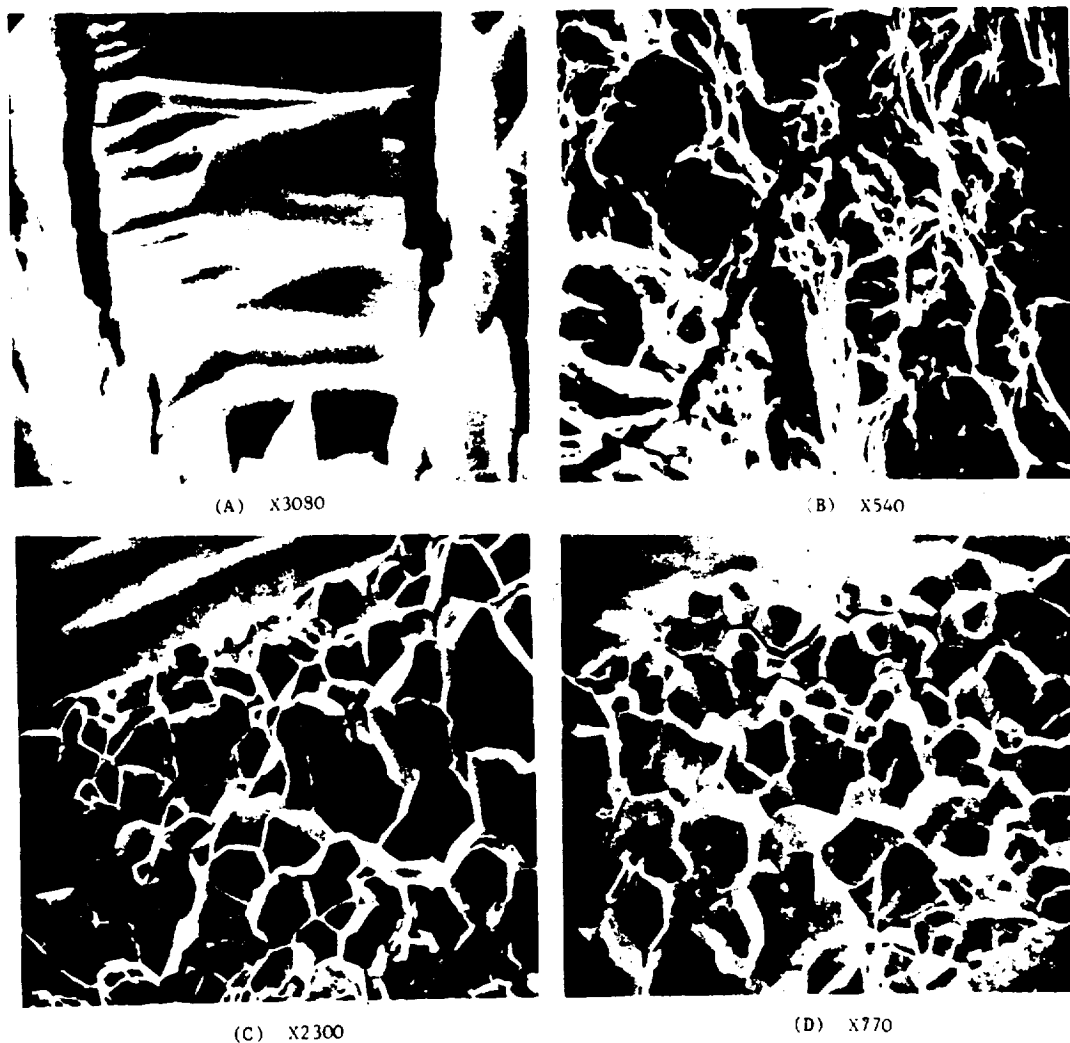


FIGURE 14. S.C.C. Specimens of Ti-5Al-5Sn-5Zr Rod and Crystal Bar Titanium Foil in methanolic Solutions Containing 0.01N HCl, Stressed to 85% Y.S. and 75% Y.S. respectively, and Corrosion Specimen of Crystal Bar Titanium Foil in same solution: (A) S.C.C., Ti-5Al-5Sn-5Zr, 0.19% H₂O, Crack Initiation. (B) S.C.C., Ti-5Al-5Sn-5Zr, 0.19% H₂O, Crack Propagation. (C) S.C.C., Crystal Bar Titanium Foil, 0.10% H₂O. (D) Free Corrosion, Crystal Bar Titanium Foil, 0.10% H₂O.

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